Ioffe Institute
6th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 22–26, 1998.

Mechanism of photoluminescence from Si-nanocrystals fabricated in SiO_2-matrix

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1 Introduction

The observation of intense visible photoluminescence (PL) of porous silicon at room temperature by Canham [1] has stimulated extensive investigation of the emission properties of different kinds of nanocrystal structures, motivated by the need to integrate optical and electronic devices on silicon chip. Silicon nanocrystals fabricated by Si ion implantation into silicon oxide with subsequent thermal annealing are promising candidates as visible light emitters. In these nanocrystals the visible and near-infrared PL was observed [2, 3, 4]. However only the luminescence in the 1.5–1.7 eV range is considered to be connected with nanocrystals themselves [4].

Recently, two possible mechanisms of radiative recombination in silicon nanocrystals were discussed in the literature [3, 5]. These are the recombination between quantum confinement levels, and recombination via levels of defects localized either inside the nanocrystals or on the nanocrystal–amorphous silicon oxide interface.

In this work we report the results of an experimental investigation of Si-nanocrystals PL kinetics, excitation power and temperature dependencies. The goal of this study is to establish the mechanism of radiative recombination in Si-nanocrystals fabricated by thermal annealing of SiO_2 layers implanted with Si.

2 Experimental details

2.1 Sample preparation

To prepare silicon nanoclusters, 500 nm-thick SiO_2 films thermally grown on (100) Si wafers were implanted with Si ions. Double implantation with energies of 100 keV and 200 keV at a target temperature of $-50°C$ was used (penetration depth 100–300 nm). The films were then subjected to transient heat treatment at 1200°C for 1 s in an Ar ambience, and finally annealed at 400°C for 0.5 h in an N_2 with 5% H_2 to improve the quality of the interfaces between the Si clusters and the surrounding oxide. The results of TEM and Raman scattering investigations evidenced the formation of crystalline silicon clusters with an average size of 3.5 nm [4].

2.2 Photoluminescence measurements

Photoluminescence measurements were carried out using a double diffraction grating monochromator equipped with a cooled S-1 photomultiplier operated in photon counting mode. An Ar^+ laser operating at a wavelength $\lambda = 488$ nm was used for excitation of *cw* PL with a maximum power density of 2.5 kW/cm^2, while for transient PL excitation a frequency-doubled Q-switched Nd:YAG laser ($\lambda = 532$ nm, pulse duration 0.15 μs, peak power density 0.4 kW/cm^2) was used.

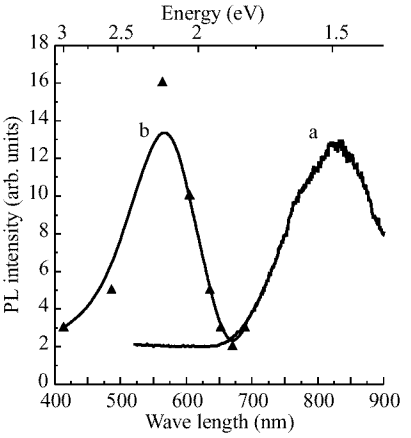

Fig. 1. The PL spectrum of the Si-nanocrystals (a) and the simulated PL spectrum (b).

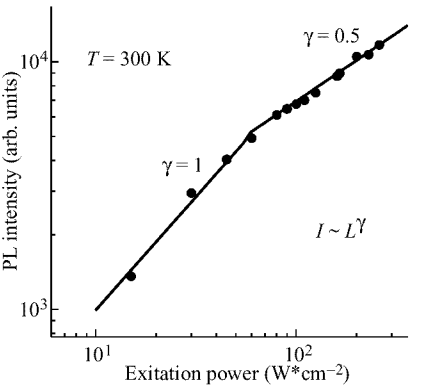

Fig. 2. The dependence of PL intensity of the Si-nanocrystals on the excitation power at room temperature.

3 Results

In Fig. 1 a typical room-temperature PL spectrum of silicon nanocrystals is shown. The spectrum comprises an asymmetrical wide band (width of about 300 meV) peaked at 1.5 eV. Also in this figure the distribution of sizes of silicon nanocrystals observed by TEM, and a simulated PL spectrum calculated on the basis of the distribution of sizes by the method suggested in [6] are shown. It is seen that the band in the simulated spectrum is shifted to shorter wavelengths in comparison with the experimental one and has its maximum at 2.1 eV, and also that the shapes of the simulated and experimental spectra are different.

In Fig. 2 the dependence of the PL intensity (I_{PL}) on excitation power (L) together with the approximation of this dependence by a power-law function $I_{PL} \sim L^{\gamma}$ is shown. Two parts with different slopes are observed in the dependence. At low excitation power the dependence is linear, while at high powers it becomes sublinear with $\gamma = 0.5$. It is necessary to note that the shape of the PL spectrum does not change with excitation power.

In Figs. 3,*a* and *b* the dependencies of the PL band position and intensity on temperature are shown, respectively. For comparison in Fig. 3,*a* the temperature dependence of the band gap of bulk silicon is shown. It is seen that the PL peak position changes only slightly with temperature as compared with the change of the bulk Si band gap. The PL intensity decreases by approximately 1.5 times with temperature increased from 80 to 300 K.

In Fig. 4,*a* transient PL spectra taken at room temperature are shown. It is seen that with increasing the delay time after the excitation pulse the shape of the spectrum does not change. In Fig. 4,*b* the decay curve of PL integrated over the spectrum is shown. The curve is approximated by a stretched exponential function $I_{PL} \sim \exp[-(t/\tau)^{\beta}]$ with a characteristic decay time $\tau = 20$ μs and a power $\beta = 0.43$.

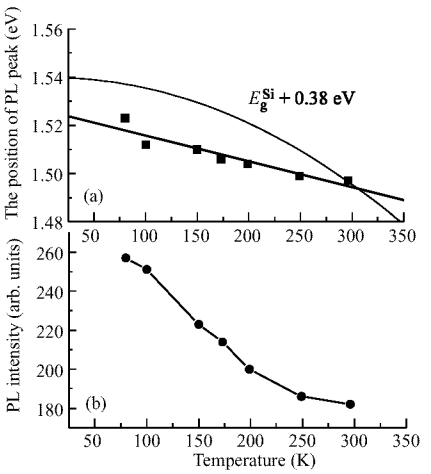

Fig. 3. (a) The temperature dependence of the maximum PL band from Si-nanocrystals and the band gap of the bulk Si. (b) The temperature dependence of PL intensity from Si-nanocrystals.

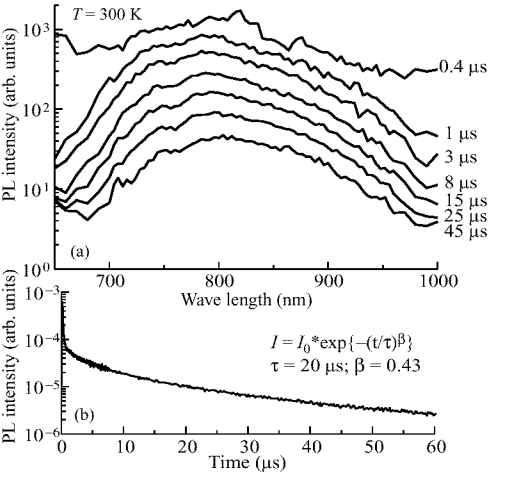

Fig. 4. (a) Time-resolved PL spectra of Si-nanocrystals. (b) The decay curve of integral PL intensity.

4 Discussion

The above results support the assumption that radiative recombination in silicon nanocrystals is governed by defect levels. The following observations point to this conclusion. Firstly, the energy of radiative recombination is less than the expected energy of optical transitions between the quantum-confined levels (see Fig. 1). Secondly, the sublinear dependence of PL intensity on the excitation power indicates that the recombination is mediated by some localized centers which saturate at high excitation powers [7] and thus let charge carriers recombine via competing nonradiative channels. In contrast, a sublinear dependence is not expected for the recombination between quantum-confined levels in nanocrystals.

Thirdly, the temperature dependence of the PL band position disagrees with that of the bulk silicon band gap, while the two dependencies should correlate in the case of recombination between quantum-confined levels in nanocrystals. Here, consideration of the effect of mechanical stress in silicon nanocrystals, which arises due to the difference of the thermal expansion coefficients of silicon and silicon dioxide, does not change the character of nanocrystal's band gap temperature dependence and results only in a correction to the band gap of about 7 meV in the temperature range from 80 to 300 K.

For centers which are strongly bound with lattice the temperature dependence of their PL band energy is different from that of the band gap. The recombination via such centers, exhibiting usually a wide PL emission, is described using the configuration diagram model [8, 9]. In this model the direction of the PL band shift with temperature is determined by the ratio of the frequencies of vibration modes in the ground and excited states of the center. In our case, the ground state frequency is higher. The slight change of PL intensity with temperature points to a high value of the thermal activation energy of the centers.

Fourthly, the absence of spectral dependence of PL kinetics seen in Fig. 4 also

points to recombination via local centers. In the case of the quantum confinement recombination model the PL decay should proceed faster on the shorter wavelength side of the spectrum because of the strong dependencies of both the recombination probability and energy of optical transitions on nanocrystal radii. The calculated lifetime of transitions with 1.5 eV energy in the quantum confinement recombination model equals to 100 μs, which is greater than our experimental data. Moreover, the quantum confinement recombination mechanism should lead to an exponential PL decay [10].

The possible centers of radiative recombination can be localized either on the Si-SiO_2 boundary or in the SiO_2 matrix. The defects in SiO_2 are well investigated and there is no evidence for the existence of centers having their luminescence in the 1.5–1.7 eV range [11, 12].

The center of recombination on the Si nanocrystal-silicon dioxide boundary responsible for 1.5 eV luminescence was considered by G. Allan et al [5]. It was attributed to a single covalent bond, for example a Si–Si bond. The calculation shows that a metastable recombination state, separated by an energy barrier from the excited state, can exist on the boundary of small nanocrystals. The nonexponetial decay kinetics is possible in such centers if the barriers between excited and metastable states of the centers have a certain energy scatter and, consequently, the probability of carrier transition from the excited to recombination state differ. In our case, since the recombination centers are localized on the boundaries of nanocrystals, the barrier height can depend on the local environment.

5 Conclusion

The luminescence properties of silicon nanocrystals formed by Si ion implantation into SiO_2 matrix and a subsequent thermal annealing have been studied. For identification of PL mechanism the dependencies of *cw* PL on temperature and excitation power density, and time-resolved PL have been investigated. Experimental results point to the mechanism of recombination via the levels of centers which are localized on the silicon nanocrystal-silicon dioxide boundary.

We are grateful to G. A. Kachurin and I. E. Tyschenko for supplying us with the samples used in this study.

References

[1] L. T. Canham, *Appl. Phys. Lett.* **57** 1046 (1990).
[2] H. Tamura et al., *Appl. Phys. Lett.* **65** (12) 1537 (1994).
[3] P. Mutti et al., *Appl. Phys. Lett.* **66** (7) 851 (1995).
[4] G. A. Kachurin et al., *Nucl. Instr. Meth.* **B 122** 571 (1997).
[5] G. Allan et al., *Phys. Rev. Lett.* **76** (16) 2961 (1996).
[6] J. B. Khurgin et al., *Appl. Phys. Lett.* **69** (9) 1241 (1996).
[7] W. Shockley and W.T. Read, *Phys. Rev.* **87** 835 (1952).
[8] R. C. O'Rourke, *Phys. Rev.* **91** (2) 265 (1953).
[9] K. K. Rebane, *Elementary theory of vibrational spectra structure of impurity centers in crystals.* M., p. 232 (1969) (in Russian).
[10] M. W. Carlen et al., *Phys. Rev.* **B 51** (4) 2173 (1995).
[11] V. A. Gritcenko, *Construction and electronical structure of amorphous dielectric and silicon MIS structures*, Novosibirsk, "Nauka", 1993 (in Russian).
[12] S. Bota et al., *Solid State Electronics* **39** (3) 355 (1996).